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CLEANING METHOD
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SPECIFICATION /395*

1. Title:

CLEANING METHOD

Abstract:

PURPOSE: To remove a stain bonded chemically or diffused in a material to be cleaned in a short time by subjecting the material to ultrasonic cleaning solution containing suspended fine SiO_2 particles having a prescribed particle size.

CONSTITUION: Fine SiO_2 particles having $\leqq$ 50 nm particle size are suspended in fuming sulfuric acid, fuming nitric acid or an organic solvent such as acetone or trichloroethylene as a cleaning solution. A material to be cleaned is subjected to ultra cleaning in the cleaning solution containing the fine SiO_2 particles. The particles hit the material on the surface and remove the stained layer without deteriorating the surface properties. Thus, the stain bonded chemically or diffused in the material is removed in a short time.

2. Claims

[CLAIM 1] Cleaning method where the material to be cleaned is subjected to ultrasonic cleaning while submerged in a cleaning solution mixed with suspended fine silicon dioxide particles having 50 nm or less diameter.

[CLAIM 2] The cleaning method stated in Claim 1 whose cleaning solution is organic solvent, such as acetone or trichloroethylene.

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* Number in the margin indicates pagination in the foreign text.

[CLAIM 3] The cleaning method stated in Claim 1 whose cleaning solution is fuming nitric acid or fuming sulfuric acid.

3. Detailed Description of the Invention

This invention provides a cleaning method under which the material to be cleaned is subjected to ultrasonic cleaning while submerged in solution mixed with particles of silicon dioxide (SiO_2). This cleaning method enables cleaning of contamination that conventional cleaning methods could not remove.

The contamination adheres to the material to be cleaned in one or more of the following 4 ways:

(1) Attraction between molecules

(2) Adherence due to static electricity

(3) Chemical bonding

(4) Diffusion into the material to be cleaned

(1) and (2) can be resolved by breaking up the attraction between the contamination and the material to be cleaned. Such contamination could be removed, for example, by ultrasonic cleaning while immersed in organic solvent or by boiling. However, chemical bonding is involved in (3) and (4), and the material to be cleaned is penetrated either by chemical reaction between contamination and cleaning material or by diffusion layer of contamination. Therefore, it was difficult for above mentioned cleaning methods to remove these types of contamination.

This was especially problematic with thin film magnetic head baseboard and semiconductor baseboard with mirror finished surfaces, which are easily susceptible to contamination diffusion. If final polishing

agents like abrasives and adhesives should cause contamination, conventional cleaning methods could not clean them completely. These types of contamination are considered quite harmful since they deteriorate head and device characteristics greatly. /396

In case of thin film magnetic heads, insulating characteristics are first obtained by depositing insulating film such as of silicon dioxide (SiO_2) on top of single-crystal or multi-crystal ferrite baseboard which has been finished to 2 nm or less surface roughness. The magnetic head is then created by building up magnetic material layer, conductive material layer and insulating material layer. If contamination is fixed on this mirror-finished surface by diffusion, even if insulating film (for example of silicon dioxide SiO_2) is deposited on the top, the insulating characteristics of this contaminated section remains relatively low compared to other section, resulting in deterioration of this characteristics. Further, the insulating film can easily detach from the baseboard since adhesion of insulating film to the baseboard is weaker at contaminated section. Thus such baseboards cannot be used for thin film magnetic heads. The same can be said about baseboards for semi-conductors.

For this reason, in order to enable re-use of baseboards whose contamination is firmly fixed and cannot be removed by conventional cleaning methods, there were two practical methods available. First cleaning method is to remove the contamination layer mechanically by re-polishing the surface of the contamination. And second cleaning method is to remove the contamination layer chemically by using etching solvent

which reacts chemically to the material to be cleaned. The first method, however, requires multiple steps such as rough polish, medium polish, and finishing polish taking up too much time. Additionally, sufficient processing margin must be allowed for under this first method since considerable thickness of the baseboard could be lost from the process. The second method posed some danger with baseboards which require high mirror-finished surface characteristics since chemical contamination removal process tend to worsen the roughness of the baseboard. This is illustrated by an example in Fig. 1 and Fig. 2. These figures compare the surface profile of mirror-finished single-crystal ferrite baseboard (Fig. 1) to the surface profile of this baseboard after it was etch-processed for 10 minutes using hydrochloric acid (Fig. 2). It is clear that the surface roughness is considerably worse after the chemical contamination removal process.

This invention provides a cleaning method that removes contamination, which could not be removed by traditional cleaning method, without changing the surface roughness and does so easily.

The uniqueness of this invention is in the cleaning method - an ultrasound cleaning method - in which the material to be cleaned is submerged in a solvent mixed with fine silicon dioxide (SiO_2) particles with diameter not exceeding 50 nm. And this cleaning method has improved cleaning effectiveness significantly.

When ultrasonic vibration is applied to fine silicon dioxide (SiO_2) particles, the kinetic energy of the fine particles causes the particles to collide with the surface of the material to be cleaned. This kinetic

energy of the fine particles breaks up binding of atoms on the closest vicinity of the surface of the material to be cleaned, which removes atoms in the surface layer as well as the contamination layer. This is the basic principle of this cleaning method. But, in order to achieve this objective without any damage to the surface characteristics (of crystalline form and surface roughness), the kinetic energy of each fine particle must be just sufficient to breaking up the binding of few atomic layers on the surface of the material to be cleaned, and the size of various particles must be kept to the minimum.

In Fig. 3, changes of surface roughness of single-crystal ferrite baseboards were observed for various particle sizes used in the cleaning solvent. The surface of this baseboard was originally finished to surface roughness of 2 nm. The baseboard was submerged in acetone, mixed with suspended silicon dioxide SiO_2 particles of various diameters but of the same weight % (4 weight %), and was subjected to ultrasonic cleaning for 10 minutes. It is clear from Fig. 3 that when particles of sizes 40 - 50 nm or less were used, the surface roughness similar to the level prior to the cleaning (2 nm) was maintained. On the other hand, when the particle diameters were increased beyond that level, the post-cleaning surface roughness was observed to have increased.

Figure 4 measures the speed of surface contamination removal when single-crystal ferrite baseboard was suspended in acetone solvent mixed with silicon dioxide SiO_2 particles of various sizes and was subjected to ultrasonic cleaning. It shows that the removal speed increases as the particle diameter decreases or increases from 40 - 50 nm.

From Figs. 3 and 4, it is clear that the smaller particle diameter can better perform minute removal of the surface without deteriorating the surface characteristics of the material to be cleaned, and also that a higher removal speed can be achieved as more fine particles are engaged in the cleaning. On the other hand, if the particle size exceeds /397
40 - 50 nm, although the removal speed increases, the kinetic energy of each particle also increases causing damages to surface interior of the material to be cleaned as well as resulting in rougher surface after the cleaning process and deteriorating surface characteristics. From these observations, it is clear that the fine particles of sizes 50 nm or less should be used for cleaning, and that the best results are obtained when fine particle sizes of less than 30 nm are used.

If contamination diffusion layer exists on the surface of the material to be cleaned, the atom density and atom composition of the diffusion layer is different from those of the non-diffusion layer. For this reason, when ultrasonic vibration of fine particles collide with surface of the material to perform a micro removal of the surface, there will be slight difference in the speeds of removal between diffusion layer and non-contamination layer, and this difference will result in minute surface level difference of the material to be cleaned. Normally, diffused materials in the diffusion layer (for example, fats and resins) tend to prevent micro removal of atom order, causing slow down in the speed of removal. Thus, in order to obtain average removal speed on contamination layer and non-contamination layer, it was necessary to dissolve and remove contamination diffusion materials on the top surface of the material to

be cleaned. This is why organic solvents like acetone or trichloroethylene are used for substance to dissolve fine silicone dioxide particles in them. In other words, as ultrasonic vibration of fine silicon dioxide particles cause them to collide with the material to be cleaned, breaking up atomic bond of few atomic layers and performing micro removal, the cleaning organic solvent dissolves and removes contamination diffusion materials as they rise to the top surface. By repeating this cycle, it is possible to perform micro removal on contamination diffusion layer and non-contamination layer at the same speed.

In case of thin film magnetic head baseboards made from ferrite materials, it is possible to completely remove contamination diffusion on baseboard surface by ultrasonic cleaning while the baseboards are submerged in organic solvents like acetone and trichloroethylene mixed with fine silicon dioxide particles. Similarly, with semi-conductor baseboards made from single-crystal silicone, just as with thin film magnetic baseboards, it is possible to achieve the desired result by using organic solvent for dissolved substance. However, since silicone has an excellent chemical resistance characteristic, it is possible to remove contamination from materials like high polymer easily (within about 2 minutes) by using fuming nitric acid or fuming sulfuric acid for dissolved substance.

This invention has limited fine particles for mixing in cleaning solvent to those of silicon dioxide (SiO_2). The reason for that is as follows. Silicon dioxide is a chemically very stable and would not react to most of acid and alkalis (as exceptions, it does react to fluorinated

acid solvent and fluorinated nitric acid solvent). In contrast to this, if particles of magnesium oxide MgO or red oxide Fe_2O_3 are used as fine particles for cleaning, if hydrochloric acid or nitric acid is used for dissolved substance, chemical reaction happens between such materials, dissolving fine particles in the dissolved substance and making them useless for cleaning purpose.

Further, silicon dioxide is mechanically robust and it maintains mechanical characteristics even when the particle diameter is down to minute numbers life few nm. Thus, there is no danger of such particles breaking up during ultrasonic cleaning and they maintain excellent cleaning performance over time.

The following is a detailed explanation of the cleaning method under this invention.

Figure 5 shows the result of surface profile measurement of single-crystal ferrite baseboard (for thin film magnetic heads) whose surface was finished to 2 nm roughness. This figure shows a spike (A) in the middle section of the chart due to contamination. This is due to adhesive resin, used for baseboard polishing, which stuck to the baseboard surface. Figure 6 shows the surface profile following an attempt to clean this contaminated baseboard by traditional cleaning method. The cleaning method used ultrasonic cleaning in trichloroethylene (for 15 minutes) and ultrasonic cleaning in acetone (for 15 minutes). The pre-existing spike, however, was not removed completely.

On the other hand, Fig. 7 shows the surface profile after applying the cleaning method of this invention to this baseboard. It shows that

the surface roughness of 2 nm is maintained and the contamination has been removed completely within a short time. The cleaning condition is listed here:

- Fine particles: Silicone dioxide SiO_2, particle diameter of about 7 nm
- Cleaning solvent (dissolved substance): Acetone
- Weight % of particles in total solvent: 10 weight %
- Time of ultrasonic cleaning: 5 minutes /398

An appropriate high frequency of the ultrasonic cleaning, by the way, is 20 - 50 kHz. In this example, high frequency of 30 kHz was used.

As explained thus far, this invention enables removing contamination which was difficult to remove by traditional cleaning method (for example contamination diffusion layer penetrated in the materials to be cleaned) without changing surface roughness of the material to be cleaned and within a short time.

4. Brief description of the figures

FIGURE 1 shows surface profile of single-crystal ferrite baseboard which was mirror finished. FIGURE 2 shows the surface profile of the same baseboard after chemical etching process. FIGURE 3 shows relationship between average particle size of SiO_2 particles used in the cleaning method of this invention and the surface roughness after cleaning process. FIGURE 4 shows relationship between average SiO_2 particle size and speed of surface removal. FIGURE 5 through FIGURE 7 show cleaning performance of traditional cleaning method and that under this invention. FIGURE 5 shows the surface profile of baseboard prior to cleaning. FIGURE 6 shows surface

profile of baseboard after cleaning using traditional method. FIGURE 7 shows surface profile of baseboard after cleaning using the method under this invention.

FIGURE 1

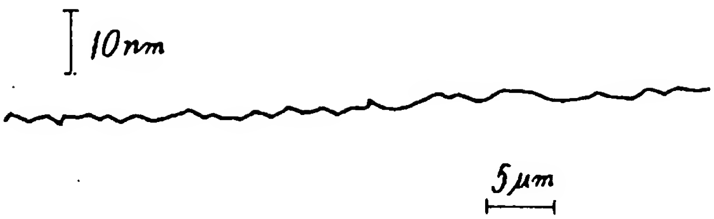


FIGURE 2

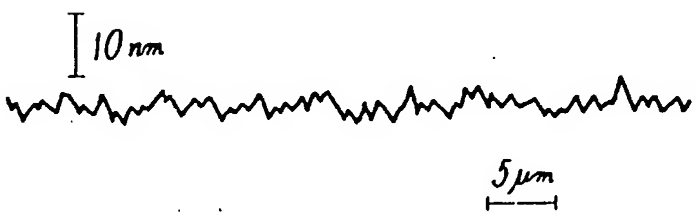
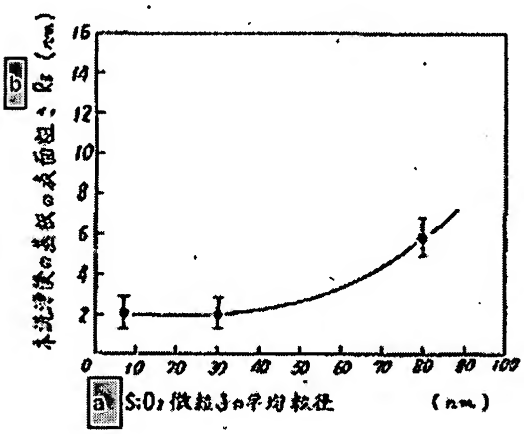
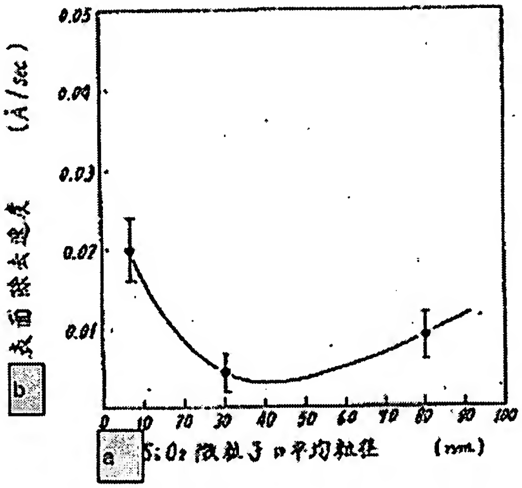


FIGURE 3



Key: (a) Average size of SiO_2 particles (nm); (b) Baseboard surface roughness of after cleaning using this method Rz (nm)

FIGURE 4



Key: (a) Average size of SiO_2 particles (nm); (b) Speed of surface removal (A / sec).

FIGURE 5

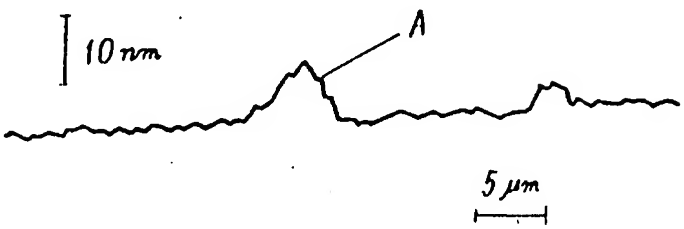


FIGURE 6

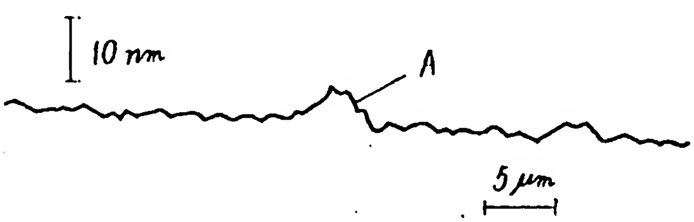


FIGURE 7